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Littel, R.J.; Filmer, B.; Versteeg, G.F.; Swaaij, W.P.M. van

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MODELLING OF SIMULTANEOUS ABSORPTION OF H_2S AND CO_2 IN ALKANOLAMINE SOLUTIONS: THE INFLUENCE OF PARALLEL AND CONSECUTIVE REVERSIBLE REACTIONS AND THE COUPLED DIFFUSION OF IONIC SPECIES

R. J. LITTEL, B. FILMER, G. F. VERSTEEG and W. P. M. VAN SWAAIJ
Department of Chemical Engineering, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

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Abstract—Numerical models, based on Higbie's penetration theory, were developed to study the effect of the coupled diffusion of ions and the effect of parallel and consecutive chemical reactions on the mass transfer rate for the simultaneous absorption of H_2S and CO_2 in aqueous solutions of (mixtures of) alkanolamines. Prior to this complicated system, gas absorption accompanied by a single reversible reaction and in the presence of an inert salt has been studied in order to determine clearly the effect of coupled ion diffusion on the mass transfer rate. From the latter model simulations it was concluded that ion diffusion and consequently ion decoupling can have a significant effect on the mass transfer rate, although a rather special set of conditions is required. Model simulations for the simultaneous absorption of CO_2 and H_2S showed that incorporation in the flux model of all relevant reactions, instead of only the direct reactions between CO_2 and H_2S and alkanolamines, only leads to more realistic concentration profiles and not to changes in absorption rate predictions for practical conditions. Correct modelling of ion diffusion does give significant though minor changes in absorption rate predictions: CO_2 absorption is reduced and H_2S absorption increased.

1. INTRODUCTION

Processes in which mass transfer is enhanced by chemical reaction are frequently encountered in process industry. The chemical reactions which can occur in such processes range from a single irreversible first-order reaction to multiple parallel and consecutive reactions. Examples of the latter case are the amine processes. In these processes acid gases like H_2S, COS and CO_2 are removed in an absorption step in which they react with a basic alkanolamine solution and subsequently these gases are released in a stripping step in which the reaction is reversed by temperature increase and pressure decrease. Obviously calculation of mass transfer rates (i.e. enhancement factors) is very important in order to make proper designs for both absorber and stripper.

Absorption of one gaseous component accompanied by chemical reaction has been studied quite extensively. In the case of a single reversible or irreversible first-order reaction analytical expressions, based on film or penetration theory, have been presented for the mass transfer rate (see e.g. Westerterp *et al.*, 1984). For simultaneous absorption of two gases in a reactive liquid or absorption of one gas accompanied by multiple reactions only for some very specific situations and conditions analytical expressions for the enhancement factor can be derived (e.g. Jhaveri, 1969; Ramachandran and Sharma, 1971). Consequently approximate analytical or numerical models must be applied to calculate the mass transfer rates.

Quite a number of approximate analytical models have been presented in literature (e.g. van Krevelen and Hoftijzer, 1948; Onda *et al.*, 1970, 1972; DeCoursey, 1974, 1982; DeCoursey and Thring, 1989; Cornelisse *et al.*, 1977; Hikita *et al.*, 1982; Asai, 1990). The major drawback of these models is that their validity limits are uncertain due to the assumptions involved. Therefore the accuracy and applicability of approximate analytical models should be checked with a numerical model (Versteeg *et al.*, 1989). In general, approximate analytical models take less computation time than numerical models and if these approximate models have been thoroughly checked this may be considered an advantage in absorber or desorber calculations.

Several numerical models which describe gas absorption accompanied by chemical reactions have been described in literature. The work of Perry and Pigford (1953) and Secor and Beutler (1967) may be regarded as pioneering in this area. Owing to the increasing availability of computation power, numerical solution of mass transfer models has received a lot of attention recently.

Versteeg *et al.* (1989, 1990) presented a numerical model which describes the absorption of a gas accompanied by multiple parallel reversible chemical reactions. The reaction schemes modelled were based on their objective to describe the absorption of CO_2 or H_2S in alkanolamine solutions. The reaction rate expressions and the reaction stoichiometry were of a generalized form. The model was shown to be able to estimate very satisfactorily the experimentally obtained absorption rates of CO_2 and H_2S in aqueous solutions of (mixtures of) alkanolamines. The same

model was applied successfully by Bosch *et al.* (1989a, b, c) to interpret literature data for the absorption of CO_2 in sterically hindered amine solutions, amine-promoted carbonate solutions and amine blends.

In the models presented by Glasscock and Rochelle (1989) for the absorption of CO_2 into aqueous MDEA solution, multiple reactions and the diffusion of ionic species were taken into account. The coupling between positive and negative ions was described by the Nernst–Planck equation. For gas absorption accompanied by a second-order reversible reaction and the CO_2 absorption in MDEA comparisons were made between the enhancement factors obtained for film theory, Higbie's penetration theory, Danckwerts' surface renewal theory and a simplified Eddy diffusivity theory.

Some numerical models which describe simultaneous absorption of CO_2 and H_2S in an alkanolamine solution have been presented in literature (Cornelisse *et al.*, 1980; Haimour and Sandall, 1983; Haimour *et al.*, 1987; Al-Ghawas and Sandall, 1988; Bosch *et al.*, 1989). The penetration theory absorption model of Cornelisse *et al.* (1980) in which interacting liquid phase reactions were taken into account, is restricted to a few stoichiometric schemes. The models of Haimour and Sandall (1983) and Haimour *et al.* (1987) describe the absorption of H_2S and CO_2 in a secondary and tertiary amine solution, respectively. They assumed irreversibility and specific reaction rate expressions for both reactions, which implies that these models are of limited use only. Al-Ghawas and Sandall (1988) describe a film theory model for the absorption of H_2S and CO_2 in a tertiary amine solution, assuming reversible reactions. The penetration theory model presented by Bosch *et al.* (1989) describes simultaneous absorption of H_2S and CO_2 in (mixtures of) alkanolamines. As they assumed reversibility, generalized reaction rate expressions and generalized stoichiometry, the general applicability of their model is only limited by the type of reactions modelled.

Apart from the direct reaction between CO_2 or H_2S and amines also some other parallel and consecutive reversible reactions take place if CO_2 and H_2S are absorbed in an aqueous amine solution. Main parallel reaction is the reaction between CO_2 and OH^-. Important consecutive reactions are the instantaneous equilibria reactions between amine and protonated amine and between bicarbonate and carbonate. Ionic species are involved in all reactions which take place in aqueous amine solutions. The diffusion of these ions may affect the mass transfer rates considerably as the concentration of ions affects the backward reaction rates. Moreover, it should be realized that ionic species do not diffuse independently of each other but that the diffusion of ions is coupled in order to maintain electroneutrality throughout the liquid. In most models presented in literature until now this coupling of the diffusion of ionic species has not been taken into account: the diffusion of ions has been modelled similar to the diffusion of neutral species and electroneutrality has been attained by applying a mean ion diffusivity. Referring to this approach as modelling of ion diffusion is rather confusing. It is preferable to reserve the term modelling of ion diffusion to those models in which, in order to maintain electroneutrality, the coupling of the diffusion of ionic species is explicitly taken into account. In the model of Glasscock and Rochelle (1989) for the absorption of CO_2 in an aqueous tertiary amine solution, the diffusion of ionic species has been modelled correctly.

In the present work, mass transfer accompanied by a single reversible reaction and in the presence of an inert salt has been studied prior to the much more complicated system of simultaneous absorption of H_2S and CO_2. The absorption was modelled according to Higbie's penetration theory, taking into account the coupled diffusion of ionic species. In this relatively simple model system it was possible to study uniquely the effect of ion diffusion and ion decoupling on the mass transfer rate.

In the present work also, a numerical model, based on Higbie's penetration model, is presented for the simultaneous absorption of H_2S and CO_2 in a mixture of primary/secondary and tertiary amines. All relevant reactions including some instantaneous equilibria reactions have been incorporated in the model. The coupling of the diffusion of ionic species is described by the Nernst–Planck equation. The reaction rate expressions used are of a generalized form.

In order to investigate the influence of ion coupling and parallel and consecutive reversible reactions on mass transfer rates calculated, the present model was compared to two somewhat less rigorous models. In one of these models the diffusion of ionic species was described by assuming equal diffusivities for all ionic species, whereas the same reaction scheme was modelled as in the complex model. In the other model only the direct reactions between the amines and H_2S and CO_2 were taken into account. In this model equal diffusivities for all ionic species were assumed also. This latter model is identical to the model presented by Bosch *et al.* (1989).

2. THEORY

In this section the reaction scheme and model equations applied for the modelling of simultaneous absorption of H_2S and CO_2 in (mixtures of) amines will be described. The same mathematical approach was used for the model system, given by reaction scheme (22)–(24), which describes mass transfer accompanied by a single reversible reaction and in the presence of an inert salt.

2.1. *Reaction scheme*

If CO_2 and H_2S are simultaneously absorbed in a solution of a primary or secondary amine and a tertiary amine, the following reactions will occur:

$$CO_2 + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \quad (1)$$

$$CO_2 + 2R_2NH \leftrightarrow R_2NH_2^+ + R_2NCOO^- \quad (2)$$

$$CO_2 + OH^- \leftrightarrow HCO_3^- \quad (3)$$

$$H_2S + OH^- = HS^- + H_2O \quad (4)$$

$$HCO_3^- + OH^- = CO_3^{2-} + H_2O \quad (5)$$

$$R_3NH^+ + OH^- = R_3N + H_2O \quad (6)$$

$$R_2NH_2^+ + OH^- = R_2NH + H_2O \quad (7)$$

$$H_3O^+ + OH^- = 2H_2O \quad (8)$$

$$HS^- + OH^- = S^{2-} + H_2O. \quad (9)$$

Reactions (1), (2), (3) are finite-rate reactions. The direct reaction between CO_2 and H_2O can be neglected if either reaction (1) or (2) take place. Reactions (4)–(9) are assumed to be instantaneous with respect to mass transfer as they involve only a proton transfer. In the numerical models instantaneous equilibria reactions are modelled as finite-rate reactions with very high reaction rate constants. This equilibrium condition is easily checked with the calculated concentration profiles:

$$H_2S + R_3N = R_3NH^+ + HS^- \quad (10)$$

$$H_2S + R_2NH = R_2NH_2^+ + HS^-. \quad (11)$$

The direct reactions (10) and (11) between H_2S and alkanolamines are implicitly included in the reaction scheme (1)–(9), as reactions (10) and (11) can be regarded as a combination of the instantaneous equilibrium reaction (4) with the instantaneous equilibria reactions (6) and (7), respectively.

2.2. *Model equations*

In the present work the phenomenon of mass transfer accompanied by chemical reactions was modelled according to the penetration theory of Higbie. The effect of the electrostatic potential gradient on the diffusion of ionic species was also taken into account. This yields the following partial differential equation for each component i:

$$\frac{\partial C_i(x,t)}{\partial t} = D_i \frac{\partial^2 C_i(x,t)}{\partial x^2} - z_i D_i \frac{RT}{F} \frac{\partial(\Phi(x,t)\, C_i(x,t))}{\partial x} + R_i(x,t). \quad (12)$$

In eq. (12), Φ represents the electrostatic potential gradient, which couples the diffusion of ionic species. Under the assumption of dynamic electroneutrality ($\sum z_i J_i(x,t) = 0$) and the Nernst–Einstein equation (Newman, 1973), Φ can be expressed as a function of ion concentrations and ion diffusivities:

$$\Phi(x,t) = \frac{F}{RT} \frac{\sum_{q=1}^{NC} z_q D_q \frac{\partial C_q(x,t)}{\partial x}}{\sum_{q=1}^{NC} z_q^2 D_q C_q(x,t)}. \quad (13)$$

For one of the ionic components, eq. (12) is replaced by the static electroneutrality condition (14) in order to maintain electroneutrality throughout the mass transfer zone:

$$\sum_{i=1}^{NC} z_i C_i(x,t) = 0. \quad (14)$$

Together with appropriate initial and boundary conditions the set of eqs (12)–(14) gives a unique solution.

The initial condition for each component i is given by eq. (15):

$$t = 0 \; x > 0: \quad C_i(x, t=0) = C_{i,\text{bulk}}. \quad (15)$$

The boundary condition at the bulk side for each component i is given by:

$$t > 0 \; x = \infty: \quad C_i(x = \infty, t) = C_{i,\text{bulk}}. \quad (16)$$

The $C_{i,\text{bulk}}$ in eqs (15) and (16) follows from either a mass balance for the bulk of the liquid or the assumption of equilibrium in the liquid bulk. In the present work the latter assumption is used.

The boundary condition at the gas–liquid interface for the volatile components (H_2S and CO_2) is given by:

$$t > 0 \; x = 0: \quad -D_i \left[\frac{\partial C_i(x,t)}{\partial x}\right]_{x=0} = k_{g,i}\left[C_{g,i} - \frac{C_i(x=0,t)}{m_i}\right]. \quad (17)$$

The boundary conditions at the gas–liquid interface for the non-volatile neutral and ionic species are given by eqs (18) and (19), respectively:

$$t > 0 \; x = 0: \quad -D_i \left[\frac{\partial C_i(x,t)}{\partial x}\right]_{x=0} = 0 \quad (18)$$

$$t > 0 \; x = 0: \quad z_i D_i \frac{RT}{F} [\Phi(x,t)\, C_i(x,t)]_{x=0} - D_i \left[\frac{\partial C_i(x,t)}{\partial x}\right]_{x=0} = 0. \quad (19)$$

The production (or reaction rate) terms $R_i(x,t)$ are non-linear. Consequently eqs (12)–(19) render a set of non-linear coupled partial differential equations, which can only be solved numerically.

2.3. *Numerical treatment*

The set of partial differential equations represented by eqs (12)–(19) were solved numerically by means of a discretization technique. Before discretization several transformations were carried out in order to enhance the calculation efficiency and, consequently, reduce calculation time. These transformations were identical to those used by Versteeg *et al.* (1989). The applied numerical technique was fundamentally the same as the method used by Cornelisse *et al.* (1980). The production terms were linearized by means of a multi-dimensional Newton–Raphson linearization.

Special care was taken to arrive at a correct discretization of the term involving the electrostatic

potential gradient. Therefore this term was rewritten in a diffusion form:

$$z_i D_i \frac{RT}{F} \frac{\partial[\Phi(x,t) C_i(x,t)]}{\partial x} = z_i D_i \sum_{q=1}^{NC} \frac{\partial}{\partial x}\left[V_i \frac{\partial C_q(x,t)}{\partial x} \right] \quad (20)$$

with:

$$V_i = \frac{z_q D_q C_i(x,t)}{\sum_{m=1}^{NC} z_m^2 D_m C_m(x,t)}. \quad (21)$$

The right-hand side of eq. (20) can be regarded as a diffusion expression with a non-constant diffusion coefficient. This diffusion expression can be discretized at the same time level as the other terms in eq. (12). In this way an efficient and consistent algorithm is obtained for the set of eqs (12)–(19).

2.4. *Models*

In the present work the objective is to study the effect of coupled ion diffusion and the effect of the relevant parallel and consecutive equilibria reactions on the mass transfer rates for simultaneous absorption of CO_2 and H_2S in an aqueous amine solution. In order to arrive at this objective several more or less complex flux models were developed.

Model I

In this flux model the reaction scheme given by eqs (1)–(7) has been incorporated. The chemical reaction rate expressions applied for reactions (1) and (2) were of a generalized form.

The concentration profiles during the contact time were calculated according to the set of partial differential eqs (12)–(19). In order to study the effect of ion diffusion the option of including an inert salt in the concentration profiles calculation was also incorporated in the model. In the equilibrium model from which the boundary conditions at the bulk side and the initial conditions are obtained, equilibria (1)–(9) were taken into account.

The Higbie penetration theory model presented by Glasscock and Rochelle (1989) for the absorption of CO_2 in an aqueous MDEA solution may be regarded as a subset of the present model I.

Model II

This model is in many aspects identical to model I. Only the coupling of the diffusion of ions was not taken into account: in the model equations the term with the electric potential gradient has been omitted. Consequently electroneutrality can only be achieved by assuming equal diffusivities for all ionic species present in solution.

Model III

In this model only the direct reactions of CO_2 and H_2S with amines were taken into account. This gives the following reaction scheme:

$$CO_2 + R_3N + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \quad (1)$$

$$CO_2 + 2R_2NH \leftrightarrow R_2NH_2^+ + R_2NCOO^- \quad (2)$$

$$H_2S + R_3N = R_3NH^+ + HS^- \quad (10)$$

$$H_2S + R_2NH = R_2NH_2^+ + HS^- \quad (11)$$

Reactions (10) and (11) can be regarded as a combination of reaction (4) with reactions (6) and (7), respectively. In model III also, electroneutrality was maintained by assuming constant diffusivities for all ionic species as the term involving the electrostatic gradient was omitted. The equilibrium model used in this model to obtain the bulk phase concentrations contained the equilibria given by eqs (1)–(9). Model III is identical to the model presented by Bosch *et al.* (1989).

2.5. *Model parameters*

For the calculation of concentration profiles (and mass transfer rates) with the numerical models presented in this work a large amount of input data is required.

The forward reaction kinetics of reactions (1)–(3) have been studied extensively (see e.g. Versteeg and van Swaaij, 1988a, 1988b; Littel *et al.*, 1990b; Pohorecki and Moniuk, 1988). The backward reaction rates were estimated by the assumption that at equilibrium conditions forward and backward reaction rates are equal.

Equilibrium constants for reaction (1)–(9) are available in literature (see e.g. Perrin, 1965; Littel *et al.*, 1990a; Teng and Mather, 1989).

The diffusivities of CO_2 and H_2S in amine solutions were estimated with the N_2O-analogy. Amine diffusivities were obtained from the correlation presented by Versteeg and van Swaaij (1988c) for the diffusivity data of Hikita *et al.* (1980, 1981). Ion diffusivities for simple ions in water at infinite solution are available in literature (e.g. Newman, 1973). These diffusivities were modified using the modified Stokes–Einstein relation presented by Versteeg and van Swaaij (1988c). Diffusivities of protonated amines and carbamates were estimated from free amine diffusivities as no data are available in literature.

Solubilities of CO_2 and H_2S were obtained using the N_2O-analogy (Laddha *et al.*, 1981; Versteeg and van Swaaij, 1988c).

It is well known that reaction rate constants and equilibrium constants depend on the ionic strength. Also solubility and diffusivity are affected by the ionic strength (see e.g. Joosten and Danckwerts, 1972). Nevertheless, in the present work the effect of ionic strength on these parameters was not taken into account as this would obscure the comparisons between the three models. Moreover sufficient experimental data are lacking in order to assess all effects of the ionic strength.

3. RESULTS

3.1. *Single reversible reaction*

As simultaneous absorption of CO_2 and H_2S involves a lot of interacting phenomena, which might conceal the effects of ion coupling, absorption accompanied by a single reversible reaction and in the presence of an inert salt has been studied first as a model system:

$$A(g) \rightarrow A(l) \tag{22}$$

$$A(l) + B(l) \leftrightarrow C^-(l) + D^+(l) \tag{23}$$

$$\text{inert salt:} \quad E^-(l), F^+(l). \tag{24}$$

This model system can be regarded as a subset of model I. By variation of the salt concentration the diffusion of the ionic species which take part in reaction (23) can be affected. At very high inert salt concentrations a situation of total ion decoupling can be attained: independent diffusion of ionic species C^- and D^+. The data used in the simulations with this model system are listed in Table 1.

In Figure 1 typical concentration profiles at zero salt concentration are given. In the liquid only C^- ions and D^+ ions are present and, although their diffusion coefficients differ by an order in magnitude, these ions must diffuse at the same speed in order to maintain electroneutrality. This results in identical concentration profiles for C^- and D^+ as can be seen in Fig. 1. In Fig. 2 concentration profiles are presented for the same conditions except the salt concentration is not zero. In this case four types of ions are present in solution: the negative ions C^- and E^- and the positive ions D^+ and F^+. Consequently, although electroneutrality is maintained throughout the mass transfer zone, this does not necessarily imply that all ionic species diffuse at the same speed. This is clearly illustrated by the concentration profiles presented in Fig. 2.

In the case of reversible reactions the backward reaction rate can affect the mass transfer rate considerably (e.g. Versteeg *et al.*, 1989). For the present model system this backward reaction rate depends on the concentrations of C^- and D^+ which are a net result of reaction and diffusion. However, as the diffusion of the ionic species C^- and D^+ is influenced by the diffusion of all ionic species present in solution, the mass transfer rate of A can be affected by the presence of the otherwise inert ionic species E^- and F^+. It may be anticipated that the maximum effect of these inert ionic species will be a complete decoupling of the diffusion of the ionic species C^- and D^+. In that case the ionic species C^- and D^+ take part in the reaction diffuse according to their own diffusivity (i.e. independently from each other).

In order to investigate the influence of an inert salt on the mass transfer rate, simulations were carried out in which enhancement factors were calculated as a function of the inert salt concentration at different equilibrium constants and liquid loadings. Simulations which show the difference between total ion coupling and total ion decoupling were carried out as a function of equilibrium constant, liquid loading and driving force. The situation in which only ionic species present in solution take part in the reaction will be referred to as total ion coupling. Total ion decoupling is defined as that situation in which the ionic species take part in the reaction diffuse according to their own diffusion coefficient (i.e. independently from each other). Total ion decoupling can be attained by adding a very large amount of otherwise inert salt to the solution. At moderate inert salt concentrations partial ion decoupling occurs. The results of the simulations (total concentration of B: 2000 mol/m^3) are given in Table 2 and Figs 3–6.

In Fig. 3, the effect of the inert salt concentration on the mass transfer rate is depicted as a function of the equilibrium constant. It can be seen in this figure that with increasing salt concentration the decoupling of the diffusion of C^- and D^+ increases, resulting in

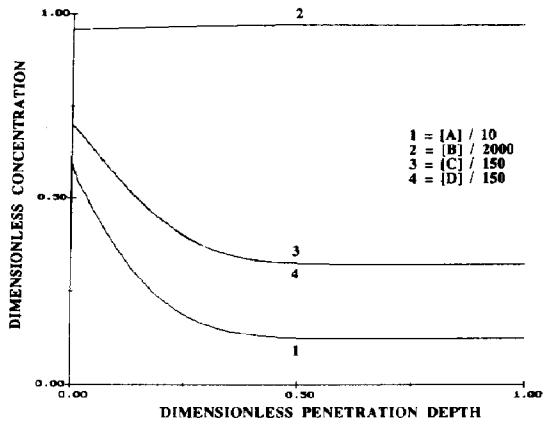


Fig. 1. Typical concentration profiles at the end of the contact time for model system without inert salt [reaction scheme (22)–(23)] ($K_{eq} = 1$, $\alpha = 0.025$, $[A]^* = 6$ mol/m^3, $[E^-F^+] = 0$ mol/m^3).

Table 1. Data for simulations with model system given by reaction scheme (22)–(24)

Reaction kinetics
Forward reaction rate: $R_{AB} = k_2[A][B]$
Backward reaction rate: $R_{CD} = k_{-2}[C][D]$
Equilibrium constant: $K_{eq} = \dfrac{k_2}{k_{-2}} = \dfrac{[C][D]}{[A][B]}$
$k_2 = 1\ \text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ $k_{-2} = k_2(K_{eq})^{-1}\ \text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$
Diffusivities
$D_A = D_C = D_E = D_F = 2.10^{-9}\ \text{m}^2\,\text{s}^{-1}$
$D_B = 1.10^{-9}\ \text{m}^2\,\text{s}^{-1}$
$D_D = 2.10^{-10}\ \text{m}^2\,\text{s}^{-1}$
Mass transfer data
$k_l = 5.10^{-5}\ \text{m}\,\text{s}^{-1}$
$k_g = 1\ \text{m}\,\text{s}^{-1}$ (no gas phase resistance)
$m_A = 0.6$
Absorption conditions

Table 2. Simulation results with model system given by reaction scheme (22)–(24)

K_{eq} [–]	α [–]	$[A]^*$ [mol/m^3]	$[A]_{bulk}$ [mol/m^3]	[Inert salt] [mol/m^3]	E_A [–]
1	0.025	6	1.2	0	6.26
				5	6.32
				25	6.51
				50	6.64
				100	6.79
				500	7.04
				∞	7.15
100	0.025	6	0	0	31.0
				5	31.0
				25	31.2
				50	31.4
				100	31.6
				500	32.2
				∞	32.6
0.1	0.0025	6	0	0	3.45
				∞	3.94
1	0.0025	6	0	0	8.25
				∞	9.91
10	0.0025	6	0	0	19.4
				∞	22.6
100	0.0025	6	0	0	32.1
				∞	33.8
1	0.0005	6	0	0	8.61
				∞	10.4
1	0.05	6	4.7	0	5.00
				∞	5.49
1	0.025	1.8	1.2	0	8.05
				∞	8.92
1	0.025	18	1.2	0	4.70
				∞	5.40
1	0.025	60	1.2	0	3.35
				∞	3.78
1	0.025	300	1.2	0	2.17
				∞	2.34
1	0.025	3000	1.2	0	1.34
				∞	1.36

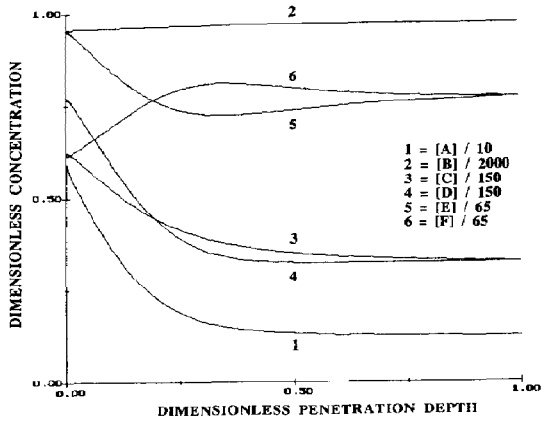


Fig. 2. Typical concentration profiles at the end of the contact time for model system with inert salt [reaction scheme (22)–(24)] ($K_{eq} = 1$, $\alpha = 0.025$, $[A]^* = 6$ mol/m^3, $[E^- F^+] = 50$ mol/m^3).

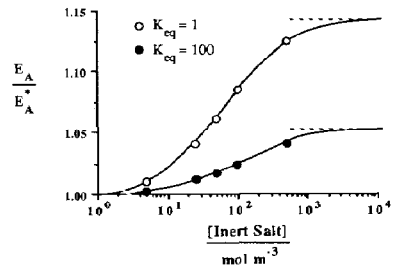


Fig. 3. Effect of the inert salt concentration on the mass transfer rate as a function of the equilibrium constant ($\alpha = 0.025$, $[A]^* = 6$ mol/m^3, dotted line: total ion decoupling).

higher mass transfer rates. Finally, at very high inert salt concentrations, the maximum of total ion decoupling is reached. Figure 4 shows that the effect of total ion decoupling on the mass transfer first increases and subsequently decreases with increasing equilibrium constant. The increase can be explained from the increasing concentrations of the ionic products C^- and D^+ with increasing equilibrium constant. As a result of the higher ion concentrations the transport of ions gets more diffusion limited and the mass transfer rate gets more affected by ion decoupling. The subsequent decrease of the effect of ion decoupling with further increase of the equilibrium

constant can be explained from the increasingly irreversible character of the reaction with increasing equilibrium constant. This causes a decrease of the effect of the backward reaction on the mass transfer rate and consequently a decrease of the effect of ion decoupling. Summarizing, it can be concluded that ion decoupling has no effect if the equilibrium constant is either very small or very large, and if the equilibrium constant increases from very small to very large the effect of ion decoupling first increases as the diffusion of ionic reaction products becomes more limiting and subsequently decreases as the irreversible character of the reaction increases.

Figure 5 shows the effect of total ion decoupling as a function of liquid loading. It can be seen that the effect of ion decoupling decreases with increasing liquid loading. This can be explained if it is considered that the electrostatic potential gradient which is given by eq. (13) decreases with increasing ion concentrations. This reflects the effect that if the total ion concentration present in solution is increased, as a result of increased inert salt concentrations, the relative amount of ions to be transported as a result of mass transfer is decreased. Hence, in this way the effect of ion decoupling on the mass transfer rate is decreased.

Figure 6 depicts the relative effect of ion decoupling on the mass transfer rate as a function of the driving force. It is shown that the effect of ion decoupling first increases and subsequently decreases with increasing driving force. The increase of the effect of ion decoupling can be understood if it is considered that the diffusion of ions becomes more and more important with increasing driving force. If the driving force increases beyond a certain magnitude, diffusion limitation of component B occurs. This results in a reduction of the effect of ion decoupling on the mass transfer rate.

In summarizing the effect of ion diffusion and ion decoupling for the model system given by eqs (22)–(24), it can be concluded that ion diffusion and consequently ion decoupling can affect the mass transfer rate up to about 20% for the present, quite realistic, conditions. However, a rather special set of conditions is required for the occurrence of this effect; and even if this set of conditions is encountered the extent of the increase of the mass transfer rate still depends greatly on the difference in ion diffusivities, e.g. a 60% increase in mass transfer rate as a result of total ion decoupling was calculated for some situations in which the diffusivities of species C^- and D^+ differed by three orders in magnitude.

3.2. *Simultaneous absorption of* CO_2 *and* H_2S

As already argued in the theory section the simultaneous absorption of CO_2 and H_2S involves a lot of complex and interacting phenomena: reversibility, parallel reactions, consecutive equilibrium reactions, ion diffusion. Owing to this complexity it is impossible to assess systematically all individual effects on the mass transfer rates. Therefore, a comparison between the three models described in the theory section will be made for some conditions, illustrative for industrial applications. The comparison of the results of model I with those of model II will give an impression of the importance of the coupling of the diffusion of ions, and the comparison between the results of model II and model III will give a good idea of the importance of taking into account all relevant reactions. Finally the comparison between model I and model III will decide whether the latter, much simpler model is preferable in practical situations.

Simulations were carried out for two aqueous amine solutions at 298 K: a 2000 mol/m^3 MDEA solution and a mixed solution of 200 mol/m^3 MEA

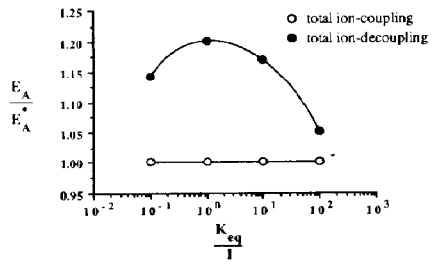


Fig. 4. Relative effect of total ion decoupling on the mass transfer rate as a function of the equilibrium constant ($\alpha = 0.0025$, $[A]^* = 6$ mol/m^3).

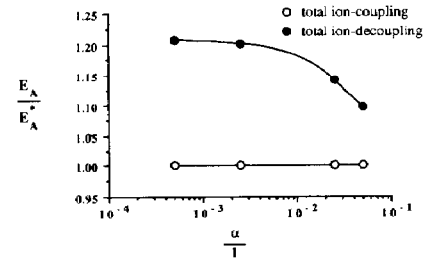


Fig. 5. Relative effect of total ion decoupling on the mass transfer rate as a function of liquid loading ($K_{eq} = 1$, $[A]^* = 6$ mol/m^3).

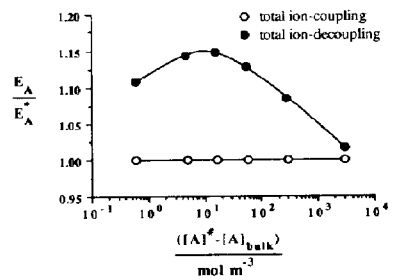


Fig. 6. Relative effect of total ion decoupling on the mass transfer rate as a function of driving force ($K_{eq} = 1$, $\alpha = 0.025$).

Table 3. Input data model simulations for simultaneous transfer of CO_2 and H_2S

System	Total amine concentration MEA [mol/m³]	MDEA [mol/m³]	Gas phase concentration C_{CO_2} [mol/m³]	C_{H_2S} [mol/m³]	Liquid phase loading α_{CO_2} [−]	α_{H_2S} [−]
Ia	0	2000	1	0	0.01	0
Ib	0	2000	1	1	0.01	0.01
Ic	0	2000	100	10	0.01	0.01
Id	0	2000	10	10	0.45	0.45
IIa	200	1800	1	0	0.01	0
IIb	200	1800	1	1	0.01	0.01
IIc	200	1800	100	10	0.01	0.01
IId	200	1800	10	10	0.45	0.45

Diffusivities (10^{10} m² s⁻¹)

Model I:

$D_{CO_2} = 9.3$ $D_{H_2S} = 9.3$ $D_{MDEA} = 4.4$ $D_{MDEAH} = 3.9$
$D_{MEA} = 6.4$ $D_{MEACOO} = 5.2$ $D_{MEAH} = 5.8$ $D_{HS} = 7.4$
$D_{HCO_3} = 5.7$ $D_{CO_3} = 4.5$ $D_{OH} = 25.6$

Models II and III:

$D_{CO_2} = 9.3$ $D_{H_2S} = 9.3$ $D_{MDEA} = 4.4$ $D_{MEA} = 6.4$

Mean ion diffusivity: $D_{ion} = 4.4$

Table 4. Simulation results for simultaneous transfer of CO_2 and H_2S

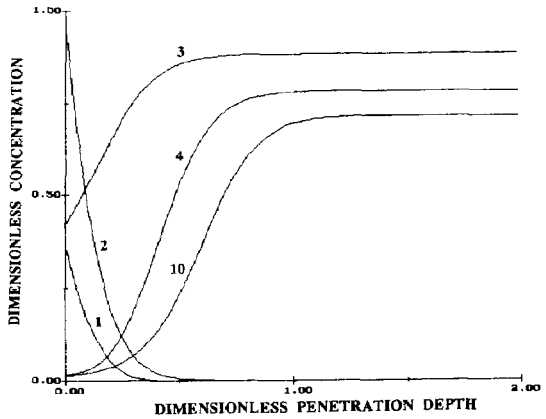
System	Model I E_{CO_2}	Model I E_{H_2S}	Model II E_{CO_2}	Model II E_{H_2S}	Model III E_{CO_2}	Model III E_{H_2S}
Ia	1.41	—	1.41	—	1.37	—
Ib	1.31	125	1.32	113	1.32	112
Ic	1.25	33.3	1.26	31.2	1.26	31.1
Id	1.02	3.75	1.02	3.44	1.02	3.42
IIa	9.73	—	9.74	—	9.72	—
IIb	5.93	144	6.41	131	6.40	130
IIc	2.56	29.7	2.67	27.3	2.67	27.3
IId	0.853	3.50	0.893	3.21	0.890	3.20

and 1800 mol/m³ MDEA. For each solvent concentration profiles and enhancement factors were calculated at various gas phase concentrations and liquid phase loadings. As all models developed in the present work offer the possibility of simulating both absorption and desorption conditions, for each solvent one set of conditions was chosen such that desorption prevailed. In all simulations gas phase resistance was negligible and a liquid phase mass transfer coefficient of 10^{-4} m s^{-1} was used. Main input data are summarized in Table 3. Chemical reaction data and physical data were obtained in the way described in the section on model parameters. The simulation results obtained from models I, II and III are given in Table 4 for all conditions presented in Table 3.

Dimensionless concentration profiles for system IIc (model I) at the end of the contact time are presented in Fig. 7. These profiles clearly show the almost complete depletion of the rapid reacting species MEA and OH^- near the gas–liquid interface. The depletion of the slower reacting MDEA is less severe. Owing to instantaneous equilibrium reactions [reactions (6) and (7)] and the presence of a less reactive amine in large quantities, protonated MEA is regenerated in the mass transfer zone, resulting in a maximum in the protonated MEA concentration. The depletion of OH^- and the instantaneous equilibrium between bicarbonate and carbonate [reaction (5)] results in a decrease of the carbonate concentration near the gas–liquid interface.

Concentration profiles for the system IIc in the presence of a relatively small amount of an inert salt are presented in Fig. 8. Comparison of Figs 7 and 8 shows that for this system (partial) decoupling of ion diffusion only has a marginal effect on the concentration profiles. This can be understood if it is considered that for system IIc production rates in the mass transfer zone are much higher than transport rates. Nevertheless it can be concluded from the inert salt profiles in Fig. 8 that ion coupling in the case of system IIc results in a reduction of the diffusion speed of negative ions and in an increase of the diffusion speed of positive ions.

For system I and II enhancement factors for CO_2 and H_2S calculated with models I, II and III are reported in Table 4. From the comparison between the results of model II and the results of model III it can be concluded that the effect of the additional



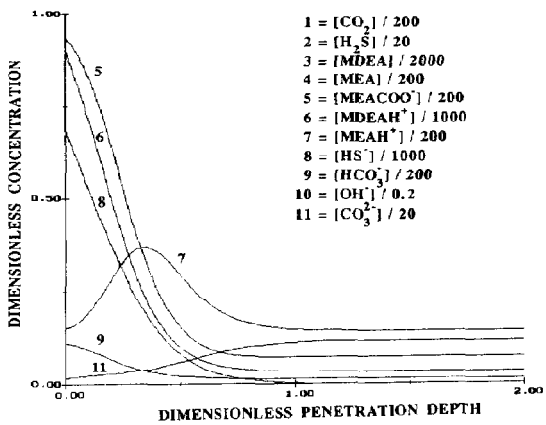
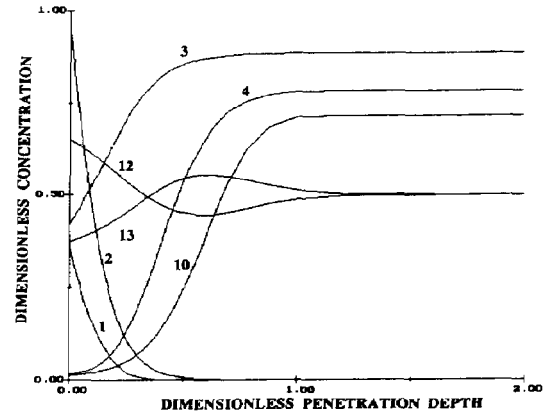


Fig. 7. Typical concentration profiles at the end of the contact time for simultaneous absorption of CO_2 and H_2S in an amine mixture (model I, system IIc, inert salt: $[E^-F^+] = 0$ mol/m^3).



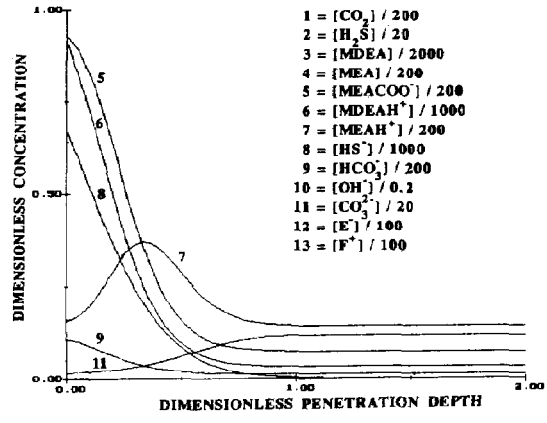


Fig. 8. Typical concentration profiles at the end of the contact time for simultaneous absorption of CO_2 and H_2S in an amine mixture with inert salt (model I, system IIc, inert salt: $[E^-F^+] = 50$ mol/m^3).

reactions which were incorporated in model II is only marginal for the present conditions. It should be pointed out, however, that the reaction between CO_2 and OH^- can have a significant contribution to the CO_2 absorption rate at very low CO_2 partial pressures (Glasscock and Rochelle, 1989). Especially in the case of reaction kinetics measurement for tertiary amines this parallel reaction should be considered very carefully (Littel *et al.*, 1990b). Apart from this exception it seems fair to conclude from the comparison between models II and III that incorporating all relevant reactions only results in a model which calculates more realistic concentration profiles.

Incorporating the coupling of the diffusion of ions in the mass transfer model does result in a significant though minor effect on the enhancement factors calculated as can be seen from the comparison between model I and model II in Table 4. For system I, only the H_2S enhancement factors are affected whereas for system II both CO_2 and H_2S absorption rates are affected. Since the mean ion diffusivity applied in model II is smaller than the effective diffusivity for HS^- in model I, the HS^- concentration near the gas–liquid interface will be lower in the latter model simulations. This results in a higher absorption rate for H_2S (higher enhancement factor) due to the smaller backward reaction rate. This higher absorption rate of H_2S will obviously be accompanied by a higher consumption of amine near the gas–liquid interface by the H_2S–amine reaction. The higher consumption of amine due to the H_2S–amine reaction may affect significantly the CO_2 absorption if the diffusion of amine towards the gas–liquid interface is limiting and if the CO_2 absorption is considerably enhanced by the reaction with amine. For system I almost no enhancement of CO_2 occurs and as a result the CO_2 absorption is almost unaffected by the higher amine consumption which is a result of taking into account ion diffusion. For system II, however, the absorption of CO_2 is enhanced considerably by the reaction with MEA and, as the diffusion of MEA is limiting, the absorption of CO_2 is reduced because of the higher amine consumption by H_2S.

It should be realized that the choice of the mean ion diffusivity in models II and II is rather arbitrary. Moreover, this mean diffusivity cannot be fitted in

Table 5. Simulation results for simultaneous transfer of CO_2 and H_2S with total ion decoupling

System	Model II		Model III	
	E_{CO_2}	E_{H_2S}	E_{CO_2}	E_{H_2S}
Ia	1.41	—	1.37	—
Ib	1.31	126	1.31	125
Ic	1.25	33.7	1.25	33.4
Id	1.02	3.78	1.02	3.75
IIa	9.73	—	9.62	—
IIb	5.98	146	5.98	145
IIc	2.61	29.8	2.61	29.7
IId	0.852	3.52	0.850	3.50

such a way that the difference between the enhancement factors calculated with model I and model II (or model III) is negligible for both CO_2 and H_2S, because an increase in calculated H_2S absorption will be accompanied by a decrease in calculated CO_2 absorption. However, based on simulations for a single reversible reaction it may be anticipated that the differences in enhancement factors calculated between a model with total ion coupling (model I) and a model with total ion decoupling will be only minor under practical conditions. In that case the enhancement factors obtained by model I can be approximated with model II or III by applying individual ion diffusivities instead of a mean ion diffusivity. In this way total ion decoupling throughout the mass transfer zone is simulated at the expense of static electroneutrality. Simulation results for models II and III with individual ion diffusivities are shown in Table 5. Comparison of the results for model I in Table 4 and the results for models II and III with individual diffusivities in Table 5 shows that a situation of almost total ion decoupling occurs for simultaneous absorption of CO_2 and H_2S in alkanolamine solutions under practical conditions. Moreover, from Table 5 it may be concluded that applying model III with individual ion diffusivities combines best calculation speed and calculation accuracy for engineering purposes. Nevertheless, for specific conditions this conclusion should be verified with the inherently more reliable model I.

The accuracy of model predictions with respect to experimental conditions is seriously limited by the accuracy of the input data. Therefore, considering the differences in calculated enhancement factors between the present models, the development of even more sophisticated mathematical flux models for gas absorption in aqueous solutions seems to be quite superfluous from a practical point of view as long as the availability of accurate input data has not caught up with the sophistication of the numerical flux models.

4. CONCLUSIONS

Numerical models were developed to study the effect of coupled ion diffusion and parallel and consecutive chemical reactions on the mass transfer rate for the simultaneous absorption of H_2S and CO_2 in aqueous solutions of (mixtures of) alkanolamines. Prior to this complicated system, gas absorption accompanied by a single reversible reaction and in the presence of an inert salt has been studied in order to determine clearly the effect of ion diffusion on the mass transfer rate.

From the simulations with the latter model system it can be concluded that ion diffusion and consequently ion decoupling can have a significant effect on the mass transfer rate, although a rather special set of conditions is required.

Simulations for the simultaneous absorption of CO_2 and H_2S have shown that correct modelling of ion diffusion leads to lower predictions for the CO_2 absorption rate and to higher predictions for the H_2S absorption rate. These changes in absorption rate predictions are generally less than 10%. Incorporation in the flux model of all relevant reactions instead of only the direct reactions between CO_2 and H_2S and the alkanolamines results in only minor changes in absorption rate predictions under practical conditions. The effect of ion diffusion can be approximated by applying individual ion diffusivities instead of a mean ion diffusivity in the simpler models. In this way total ion decoupling is simulated at the expense of static electroncutrality.

Considering the numerical models and model simulations in the present work, it must be concluded that the usefulness of such models or even more sophisticated models is hampered by the lack of sufficient and sufficiently accurate input data.

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NOTATION

D	diffusivity, $m^2\,s^{-1}$
E	enhancement factor
E^*	enhancement factor at total ion coupling
F	Faraday constant 96,489 $C\,mol^{-1}$
NC	total number of components
R_i	reaction rate for component i, mol $m^{-3}\,s^{-1}$
R	ideal gas constant, 8.314 $J\,mol^{-1}\,K^{-1}$
t	time variable, s
T	temperature, K
V	coefficient defined by eq. (21)
x	space variable, m
z	ion charge

Greek letters

α	liquid loading
Φ	electrostatic potential gradient, $V\,m^{-1}$

Subscripts/superscripts

bulk	bulk phase conditions (i.e. equilibrium conditions)
g	gas phase

i	component i
m	dummy variable
q	dummy variable
#	interface

Amine abbreviations

MDEA	N-methyldiethanolamine
MEA	monoethanolamine

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